

The Sulfur Pressure over Liquid Polysulfides

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The activity of sulfur in liquid sodium polysulfides of different stoichiometric composition was investigated in the temperature range 400–1000°C by measuring the pressure of sulfur vapour above the polysulfides by dew-point determinations. Thermodynamic analysis of the results obtained indicates that polysulfide ions of several different sizes are present in liquid polysulfides.

The existence of sodium polysulfides has been known for a long time.¹ Their phase diagrams have been determined² and their decomposition in nitrogen atmosphere has been studied.³ The sulfur activity in liquid polysulfides has, however, not been investigated. Knowledge of this activity is essential for predicting the stability of polysulfides at elevated temperatures in the presence of other compounds. In this investigation the activity of sulfur in liquid polysulfides of the stoichiometric composition Na_2S_2 , Na_2S_3 , and Na_2S_4 was investigated in the temperature range 400–1000°C by measuring the dew-point, *i.e.* the pressure of sulfur vapour above the polysulfides. Dew-point measurements have been previously used in thermodynamic studies of metal smelts.⁴⁻⁶

Standard state. As standard state the sulfur vapour S_2 of 1 atm pressure is chosen. Above 700°C the partial pressures of other sulfur forms than S_2 can be neglected.⁷ The following relation exists between the activity and the relative partial molar enthalpy H_i^M and entropy S_i^M

$$G_i^M = RT \ln P_i = H_i^M - TS_i^M$$

where G_i^M is the relative partial molar Gibbs' free energy, R the gas constant, T the temperature in °K and P_i the partial pressure, *i.e.* a measure of the activity, of sulfur. Derivation with respect to $1/T$ and T , respectively, gives:

$$\frac{\partial \ln P_i}{\partial (1/T)} = \frac{H_i^M}{R}$$

$$\frac{\partial G_i^M}{\partial T} = -S_i^M$$

Hence $H_{\text{S}_2}^M$ and $S_{\text{S}_2}^M$ can be obtained from the slopes of graphs showing $\ln P_{\text{S}_2}$ against $1/T$, and $G_{\text{S}_2}^M$ against T , respectively.

EXPERIMENTAL

Chemicals. The polysulfide was prepared from sodium sulfide and elemental sulfur. The $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, of reagent grade, was dried, first in vacuum at 120°C and then in a stream of dry hydrogen at 800°C for 15 min. The product obtained was white and contained about 97% Na_2S .

The technical granulated sulfur was considered sufficiently pure.

The dried sulfide and elemental sulfur were mixed in the required stoichiometric proportions and the polysulfide was formed during the heating to investigation temperature. After the experiments the polysulfides were analysed and found to be of the intended stoichiometric composition within the analytical error.

Analysis. The sulfide sulfur was determined acidimetrically⁸ and mercurimetrically, essentially according to Bilberg.⁹ The excess sulfur was determined acidimetrically⁸ and spectrophotometrically.¹⁰ The deviation in the results obtained by the different independent methods was less than 5%.

Dew-point measurements. About 5 g of the polysulfide studied (in a spinel crucible) was placed in a silica tube of 40 cm^3 volume that was evacuated and sealed. This tube was placed in a two-temperature-zone furnace, (Fig. 1). The lower zone containing the

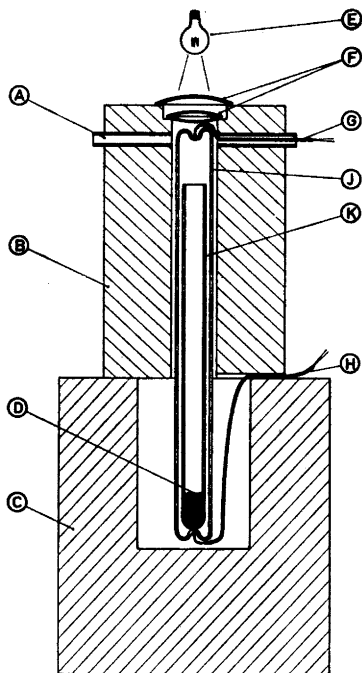


Fig. 1. The two-temperature furnace used in the dew-point measurements.

- A Tube for visual observation of the sulfur condensation;
- B "Low-temperature" furnace, electrically heated;
- C "High-temperature" furnace, electrically heated;
- D Polysulfide investigated;
- E Lamp for illumination of the sulfur condensation point;
- F Watch-glasses;
- G Thermocouple for measuring the temperature at the point of condensation;
- H Thermocouple for measuring the temperature of the polysulfide;
- J Ampoule of silica;
- K Crucible of spinel ($\text{MgO}\cdot\text{Al}_2\text{O}_3$).

polysulfide was heated to the investigation temperature, while the upper zone was heated to a temperature above the dew-point. The temperature of the upper zone was then slowly decreased, until droplets of sulfur started to condense. The dew-point was checked by repeated heating and cooling of this cold zone. The dew-points measured had a standard deviation of 2°C . The condensation temperatures (dew-points) obtained were transformed to sulfur vapour pressures according to literature data (Fig. 2). The sulfur vapour in the cold zone is a mixture of S_2 , S_8 , and S_6 , but in the hot zone (above 700°C) it consists mainly of S_2 .⁷ It is assumed that the sulfur vapour is in equilibrium in the hot as well as in the cold zone and that the total sulfur pressure is equal in the two zones. The effect

of thermal diffusion and the opposite effect of convection, as a result of differences in the density of sulfur vapour of different temperatures, were thus neglected.

Apparatus. The two-temperature-zone furnace (Fig. 1) was a combination of a crucible type and a vertical tube type furnace. The tube type furnace had besides the main winding a small one which surrounded the sulfur condensation spot at the top of the furnace. This winding was used for small and quick temperature adjustments in order to make sure that this spot was the coldest one in the furnace.

The temperatures were measured by chromel-alumel thermocouples. One thermocouple measured the temperature of the silica surface outside the condensation spot at the top of the tube. The temperature of the lower furnace was measured by two thermocouples, the readings of which deviated less than 0.2 mV, corresponding to 5°C. The temperature of the lower furnace was controlled $\pm 5^\circ\text{C}$, by a thermostat, which regulated the voltage to the furnace between two adjustable values. The temperature of the upper furnace was varied by adjusting a transformer by hand.

In dew-point measurements the temperatures of the liquid polysulfide and the condensing sulfur vapour are of interest. During the experiments only the temperatures outside the silica tube in the two furnaces were determined. The temperature differences between in- and outside of the silica tube were measured in a nonevacuated calibration tube with inlets for thermocouples. Aluminium oxide powder was used as a model substance for the polysulfides, which are easily oxidized in contact with air. The difference between the temperature of the aluminium oxide in the crucible and the temperature outside the silica tube in the lower furnace was less than 5°C. The difference between the temperatures measured outside and inside the tube at the condensation spot was found to be negligible.

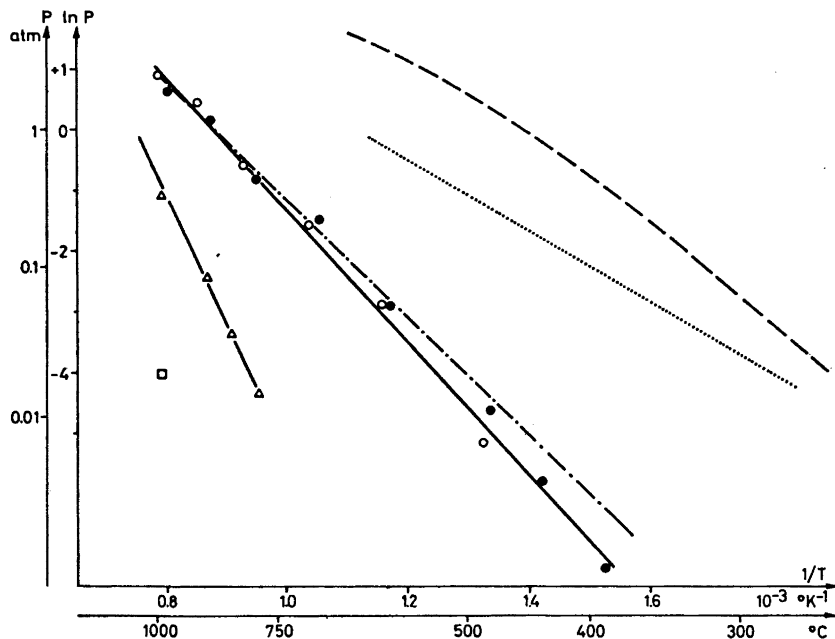


Fig. 2. The natural logarithm of the pressure of S_2 , in atmospheres, over sodium polysulfides of different stoichiometric composition plotted against the inverse of the absolute temperature. The corresponding relationship for pure molten elemental sulfur⁷ is given as (.....). The total sulfur pressures over molten elemental sulfur⁷ (---) and Na_2S_4 (- · -) are given for comparison. Over Na_2S_2 and Na_2S_3 $P_{\text{S}_2} \approx \sum P_{\text{S}_n}$. Stoichiometric composition: Na_2S_4 ○ ●, (two independent experiments); Na_2S_3 △; Na_2S_2 □.

RESULTS

The sulfur dew-points measured over polysulfides are given in Table 1. In Figs. 2 and 3 P_{S_2} and $RT \ln P_{S_2}$ are plotted against $1/T$ and T , respectively. The corresponding data for molten elemental sulfur⁷ are given for comparison. At these temperatures elemental sulfur consists mainly of chain molecules.¹¹ The relative partial enthalpies and entropies obtained are given in Table 2.

Table 1. The sulfur dew-points and the total sulfur pressures obtained for the gas-phase over sodium polysulfides of different stoichiometric composition and temperature.

Stoichiometric composition	Temperature of polysulfide °C	Dew-point °C	ΣP_{S_n} atm.
Na_2S_2	985	255	0.018
	990	375	0.34
Na_2S_3	880	310	0.086
	830	275	0.036
	775	245	0.013
	1005	530	2.59
Na_2S_4	907	476	1.46
	805	405	0.57
	695	357	0.24
	589	302	0.070
	483	230	0.0076

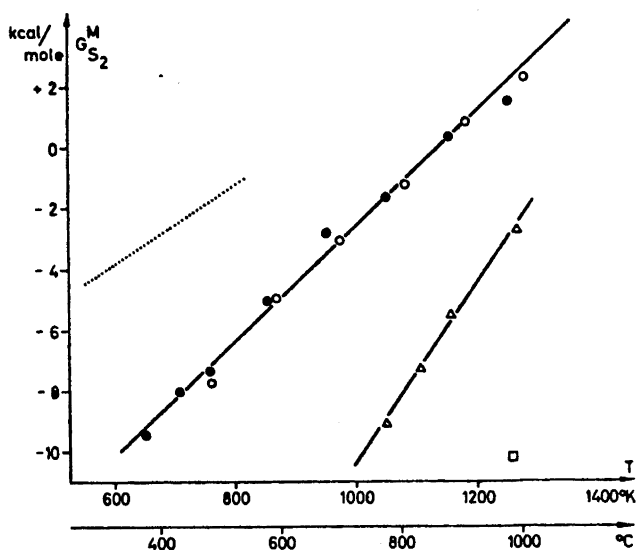


Fig. 3. The relative partial molar Gibbs free energy of S_2 , $G_{S_2}^M = RT \ln P_{S_2}$, in polysulfides of different stoichiometric composition given as a function of temperature. P_{S_2} is given in atmospheres. Signs = Fig. 2.

DISCUSSION

Kohlenmayer and Brinkman³ report that Na_2S_3 decomposes into Na_2S_2 at 730°C on boiling, which might mean that the melt was in equilibrium with a sulfur vapour of 1 atm. In the present investigation it was found that the equilibrium pressure of the sulfur vapour over molten " Na_2S_3 " at this temperature is only 0.05 atm. The difference can be explained if it is assumed that no boiling occurred in the previous investigation,³ but that sulfur was released from the surface of the melt. This is probable, as the experiments were carried out under a stream of nitrogen, the flow rate of which was not reported.

Table 2. The relative partial molar enthalpies and entropies of S_2 in molten sodium polysulfide and elemental sulfur.

Stoichiometric composition	$H_{\text{S}_2}^M$ kcal/mole	$S_{\text{S}_2}^M$ cal/mole, deg.
Na_2S_3	-41	-30
Na_2S_4	-21	-18
S_n	-11	-13

The results obtained in the present investigation cannot be explained by an equilibrium model where it is assumed that only sulfide and polysulfide ions of a single type occur as anions in the melt. Polysulfide ions of different size must be present and their relative amounts must be dependent on the stoichiometric composition of the polysulfide melt. The experimental material is, however, too small for quantitative equilibrium studies. Polysulfide ions of the type S_4^{2-} or larger ought to be present as the sulfur vapour pressure over a molten polysulfide of the stoichiometric composition Na_2S_4 was found to be considerably smaller than the vapour pressure over pure elemental sulfur of the same temperature.

The sulfur activities in molten sodium polysulfide, obtained in the present investigation, have been useful for predicting the formation and decomposition of polysulfides under conditions prevailing in the recovery furnaces of kraft pulp mills.¹²

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REFERENCES

1. Scheurer-Kestner, M. A. *Compt. Rend.* **57** (1863) 1013.
2. Pearson, T. G. and Robinson, P. L. *J. Chem. Soc.* **1930** 1473.
3. Kohlenmayer, E. J. and Brinkman, H. *Z. anorg. allgem. Chem.* **299** (1959) 182.
4. Birchenall, C. E. and Cheng, C. H. *J. Metals* **185** (1949) 428.
5. Hargreaves, R. *J. Inst. Metals* **64** (1939) 115.
6. Staffansson, L.-I. *Acta Chem. Scand.* **21** (1967) 2298.

7. Braune, H., Peter, S. and Neveling, V. *Z. Naturforsch.* A 6 (1951) 32.
8. Ahlgren, P. *Svensk Papperstid.* 70 (1967) 730.
9. Bilberg, E. *Norsk Skogind.* 12 (1958) 470.
10. Teder, A. *Svensk Papperstid.* 70 (1967) 197.
11. Tobolsky, A. and Eisenberg, A. *J. Am. Chem. Soc.* 81 (1959) 780.
12. Teder, A. and Tiberg, J. *To be published.*

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